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Ref. Contract No. N00014-96-C-0261

Please find enclosed the second report on SBIR contract No. N00014-96-C-0261, entitled Engineered GaN Substrates. During this time period we have investigated post-growth substrate removal from the GaN epitaxy. If you have any questions please do not hesitate to call.

Sincerely,

Glenn Solomon

Glenn S. Solomon

enclosure

CBL Corporation

SBIR Contract No. N00014-96-C-0261

Second report

September 9, 1996

1.0 Summary

This the second report of CBL's progress on its Phase I SBIR contract. During the first reporting period, CBL was focused on establishing a working company structure. This included hiring personnel, developing a business structure and detailing a research plan. In this period CBL has begun conducting GaN crystal growth and fundamental etching experiments. The goal of this SBIR funded project is to develop an in-situ etching technique for substrate removal; however, while the process is in the design phase we have conducted ex-situ etching studies for post growth substrate removal. These results are discussed in this report.

Two types of substrates were used. First, a substrate of (111) oriented Si was used, and second, a substrate composed of a thin layer of SiC deposited on (100) Si was used. We used the Si substrate with the SiC deposition to investigate a better lattice matched substrate and to increase the selectivity of the substrate etching process. In addition, the (100) Si may have different etching properties than the (111) Si. In the interests of cost and simplicity we hope the Si wafer without the SiC deposition could be selectively etched, while the shear thickness of the GaN epitaxy would diminish the differences in crystal quality due to the poorer lattice match of the Si substrate.

Our growth results indicate that there is little difference in crystal quality between the GaN deposited on Si and the SiC/Si substrates. Photoluminescence (PL) and X-ray diffraction (XRD) were used as characterization tools. In both cases, the PL results only show bandedge luminescence, while the XRD linewidths of the (0002) GaN are 30 arcmin. Our etching results indicate that selectively etching the (111) Si substrate is difficult. This is a surprise because of the robust nature of GaN; however, (111) Si is much more resistant to wet etching than the more typical (100) Si. PL and XRD characterization show that the GaN film is of the same crystalline quality after the substrate removal as before the removal.

These wet chemical etching experiments are not directly related to the gas-phase etch that we are developing. However, one of our strategies is to leave a small portion of the substrate attached to the epitaxy; a portion that is smaller than the epitaxial thickness. In this case some post-growth substrate removal will be necessary to produce a product with a completely removed substrate. Through these experiments it has also become clear that the best way to remove the Si (111) substrate is through gas-phase etching. We will aggressively pursue this process in the coming months.

The details of these wet chemical etching experiments are found below.

2.0 Results of Crystal Growth, Substrate Etching and Epitaxial Characterization

GaN epitaxial growth is not the salient aspect of this research; nevertheless, it is also a central focus in our work. Results from our first crystal growth are briefly discussed first. The work done in this reporting period focuses on the post growth, ex-situ substrate removal. These results are discussed second. The main body of this section is the last portion, the characterization section, in which the quality of the GaN is compared before and after substrate removal.

2.1 GaN Epitaxial Growth

CBL's ultimate goal is to grow GaN films on Si substrates which can be removed by gas-phase etching immediately after the growth, before cooling. As an important first step toward this goal, we have been developing the necessary techniques for growing high-quality epitaxial layers of GaN on Si substrates.

In the time since the last report, we have grown GaN epitaxy, predominantly on Si, by vapor phase epitaxy (VPE). The precursors used are gallium trichloride ($GaCl_3$) and ammonia (NH_3). Growth temperatures in the range of 1000 °C, with an $NH_3/GaCl_3$ ratio of 18 to 1, have been found to give good GaN films at a growth rate of 10 µm/hr. Typical growth time is one hour, for a film thickness of 10 µm.

Several studies have shown that lattice-matched interlayers on a substrate can improve the quality of a subsequently grown GaN film. We have therefore begun to explore the role of various interlayers. As a first step to study these interlayers, we have grown GaN epitaxially on (100) Si which has had a thin layer of SiC formed on top. Although this process involves a more expensive substrate, the SiC interlayer may offer improvements in the GaN which are worth the extra substrate costs. In addition, there may be benefits in using a (100) Si base material when etching.

2.2 Substrate Removal

Ultimately, CBL plans to etch away the Si substrate in-situ. However, it is important to investigate post growth substrate removal because it may result in a similar product, yet it is much easier to implement. In addition, some post growth etching may be

an important aspect of our process as the in-situ etch may leave some substrate residue. In order to achieve this, we grew GaN films on Si substrates and etched away the Si substrates ex-situ.

We experimented with a number of Si etches, including phosphoric acid, various mixtures of potassium hydroxide and isopropyl alcohol, and combinations of hydrofluoric acid and nitric acid. A 1:1 mixture of hydrofluoric acid and nitric acid was found to etch Si substrates effectively, but had the unfortunate side effect of etching the GaN films as well. It was found that etching of the GaN films could be avoided by covering them beforehand with Apiezon black wax. The samples were then mounted on the film side to a glass slide with black wax, so that only the backside was exposed. A "reference" piece of bare Si was mounted on the slide next to the sample. By carefully monitoring the etching of the sample and the reference piece of Si, we found that we could remove the glass slide from the acid when the Si had been etched away, but before the acid had a chance to etch the GaN film. The black wax was then dissolved in trichloroethane to release the freestanding GaN film.

While this technique proved successful for providing us with freestanding films to study, it will have to be modified if used as the main etching process for large-scale use. The etching process is not self-limiting, and must be visually monitored in order to determine the right moment to remove the film from the acid. Removal of the freestanding film from the black wax is time-consuming and places a certain amount of stress on the delicate film, which can result in tearing. In addition, the GaN films, having been cooled down from the growth temperature on a thermally mismatched substrate, contain residual stresses. We expect these problems to be obviated by the in-situ gas-phase etch technique.

2.3 GaN Characterization

In order to determine the quality of the GaN films, before and after removal from the substrate, we studied them with X-ray diffraction (XRD) and photoluminescence (PL). Both techniques offer insight into the structural quality of the films.

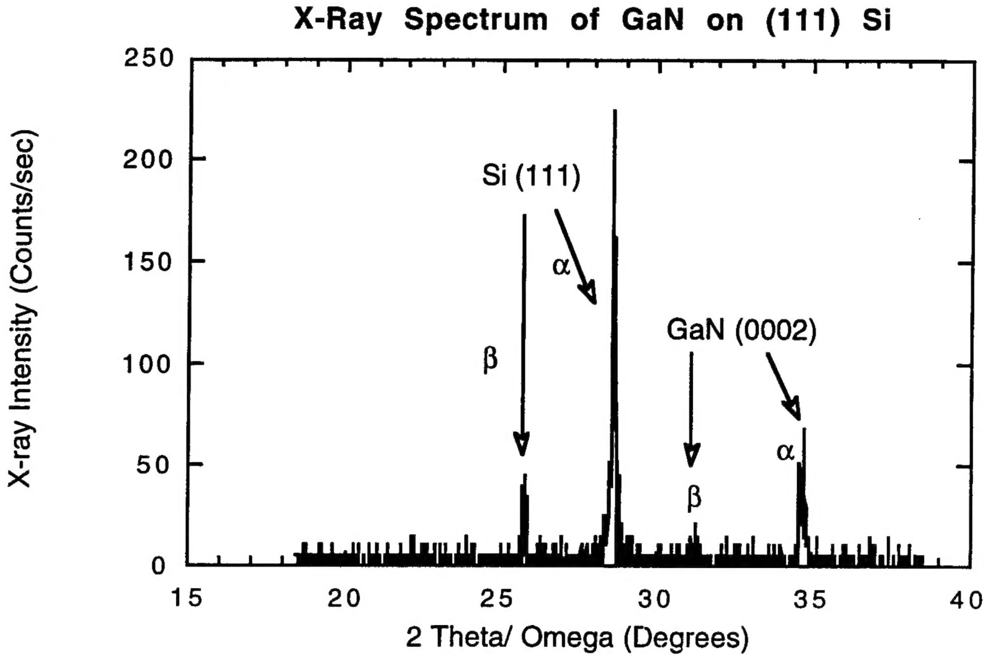

Figure 1.

Figure 1 shows a typical X-ray diffraction spectrum from a GaN film grown by vapor phase epitaxy on (111) Si. We see the GaN (0002) peak at 34°, and the Si (111) peak at 28°. (The additional small peaks are replicas from the Cu K_β X-ray line.) The full-width at half maximum (FWHM) of the GaN peak is about 30 arcminutes.

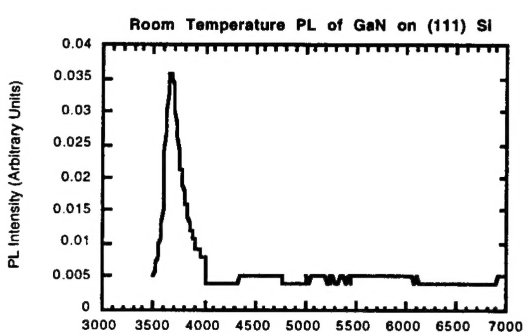

Figure 2 (a)

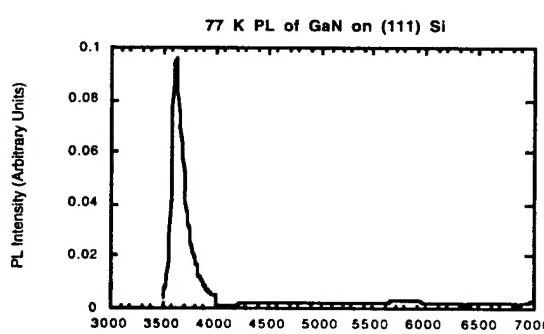

Figure 2 (b)

Figures 2 (a) and (b) show photoluminescence spectra from a GaN film grown on (111) Si. We see strong bandedge photoluminescence at both room temperature (a) and 77

K (b). In addition, we see almost none of the defect-related "yellow" luminescence that is commonly seen in GaN films. This suggests that these films are of high structural quality.

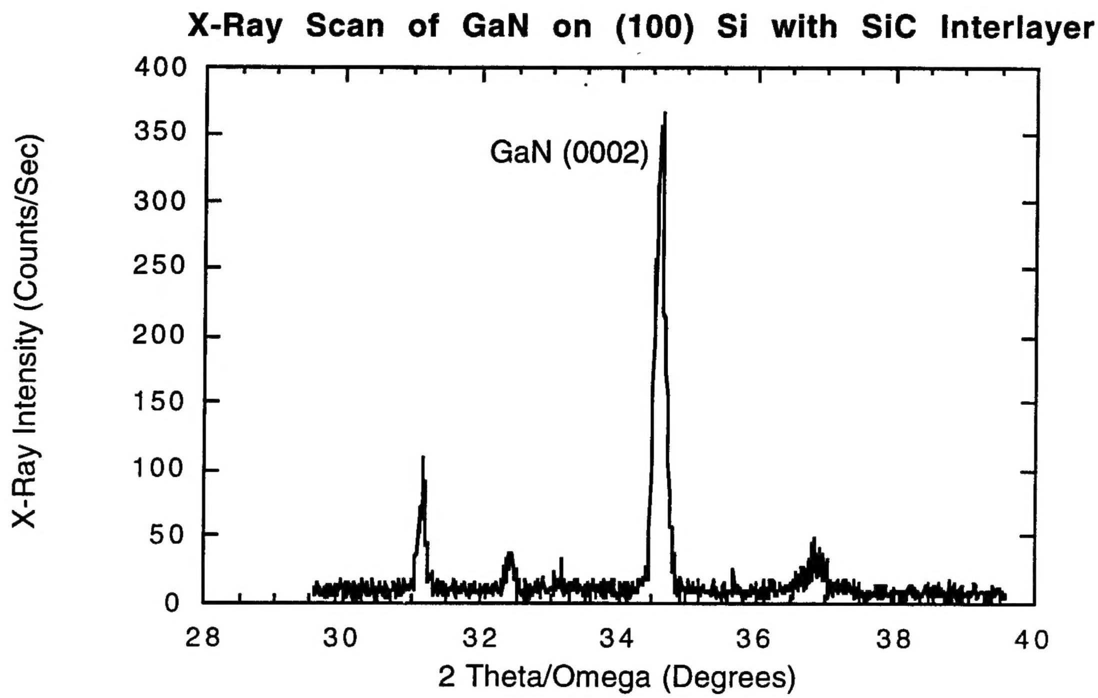

Figure 3

Figure 3 shows the X-ray diffraction spectrum from a GaN film grown by vapor phase epitaxy on (100) Si which has had a thin layer of SiC deposited on it. The FWHM is approximately 15 arcminutes, similar to the FWHM of the GaN (0002) XRD reflection.

Figures 4 (a) and (b) show the photoluminescence spectra from that GaN film. We see very strong bandedge photoluminescence at both room temperature (a) and 77 K (b). The peaks are somewhat sharper than those from the GaN grown on bare Si, and, again the non-bandedge PL is not observed.

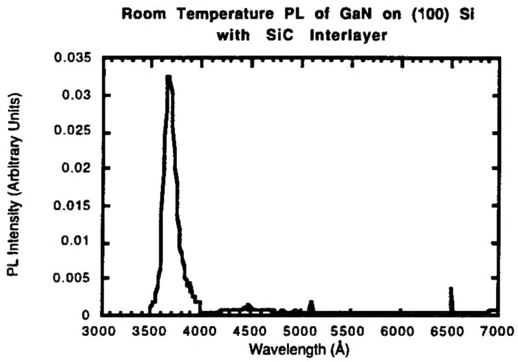

Figure 4 (a)

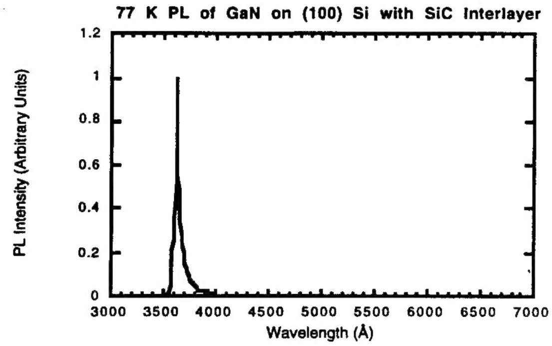

Figure 4 (b)

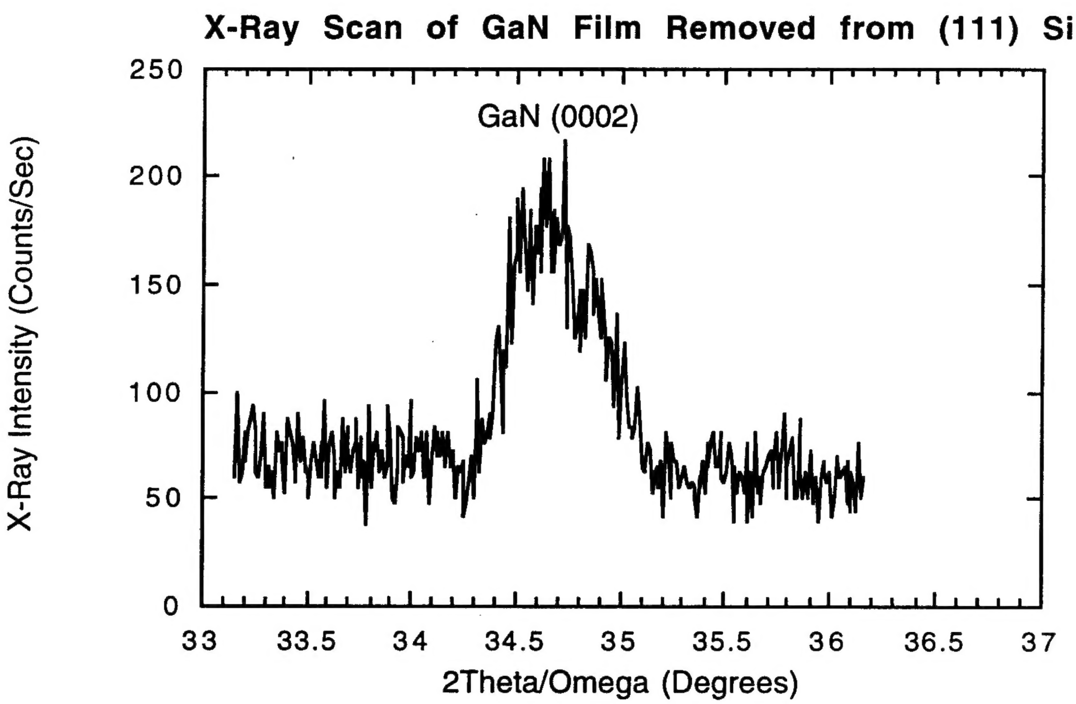

Figure 5

Figure 5 shows the X-ray diffraction spectrum from a GaN film which has been removed from a Si (111) substrate. The only peak seen is the GaN (0002) peak. The intensity of this peak is comparable to the intensity of the same peak in Figure 1. This peak shows a FWHM of about 30 arcminutes, which is again comparable to that of the same peak in Figure 1. This indicates that a GaN film which has been removed from the

substrate is of comparable quality to one still on the substrate, and that substrate removal can be effected without compromising the overall structural quality of the film.

3.0 Conclusion and Future Plans

In this work we have demonstrated the post-growth substrate removal from 10μm thick GaN epitaxy. Our substrate choice of (111) Si proved to be quite resilient to the common wet chemical etechants of Si processing because these etchants do not properly work on the (111) surface. The exceptio to this is $HF:HNO_3$ which etches both Si (111) and GaN. Using this etch good results were obtained by mounting the epitaxy-substrate with the epitaxy down and encapsulating the sample.

The GaN film is apparently undamaged by the substrate removal as the PL and XRD results were not diminished. We have learned that from an etching viewpoint the (111) Si substrate is not the best substrate choice; however, other possibilities such as GaAs, SiC or (100) Si either are too expensive (GaAs, SiC), also etch resistant (SiC), or a poorer lattice match ((100) Si).

We do not expect to encounter the same degree of difficulty in the substrate removal process using the a gaseous etch because of the high temperature. However, these wet chemical etching experiments have been important. We may incorporate the wet chemical etch as a finishing step so that the complete substrate does not have to removed in-situ. In addition, we know that the substrate removal process does not appear to damage the GaN epitaxy. Finally, we have found that although GaN is itself inert to many etches, a suitable substrate choice must also include the ease of etching of the substrate. Thus in some cases the SiC deposited on (100) Si may be a better choice.

GaN growth comparisons of the (111) Si substrate and SiC on (100) Si indicate that there is no marked difference between the two substrates. The XRD FWHM linewidths are similar and the PL spectra show only bandedge luminescence. We believe the SiC on Si did not improve the GaN growth because there is still a large 4% mismatch present and the thickness of the GaN film may mend damage due to the initial lattice mismatch of the substrate and epitaxy.

In the coming months we will continue to modify our VPE system. We will add additional gas lines for etching and rebuilt our exhaust system to handle the extra gas load. In addition, we will use this system modification period to investigate modifications to our VPE growth chamber. Within this period we expect to conduct our initial growth and substrate removal runs.